

High-pressure phase transitions of Zn_2SiO_4 : In-situ Raman spectroscopic study

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Zn and Mg have similar ionic radii, but their crystal chemical behaviors in silicates are quite different. In phase relation of Zn_2SiO_4 system, I (willemitite), II, III, IV, V (modified spinel) phases are known (Syono et al., 1971), but only V has common structure with Mg_2SiO_4 system. Neither olivine nor spinel structures exist in Zn_2SiO_4 . This difference is quite interesting in terms of crystal chemistry. Recently, we have determined crystal structures of phases III and IV, and suggested that these phases are retrograde phases (Liu et al., 2013). In order to check this possibility, first-principles DFT calculations were conducted, and pressure-induced transitions for III and IV were discovered (Kanzaki, JpGU meeting 2014). In the present study, these transitions were checked experimentally using in-situ Raman spectroscopy. Phase II was also studied, since this phase is found to transform to (metastable) spinel structure by first-principles calculations.

For observation of phase transitions, in-situ Raman spectroscopy of samples in diamond anvil cell (DAC) was conducted. Symmetric DAC was used with low-fluorescence diamond (500 micron culet). Samples of phases II, III and IV were fragments made by multi-anvil press quench experiments (Liu et al., 2013). Gasket was made of SUS301H with 250 micron thick, and 200 micron hole after indentation was made. Pressure medium was alcohol mixture for phases III and IV, and KBr for phase II. Pressure was determined by Ruby fluorescence technique. All experiments were done at room temperature.

For phase III, Raman spectrum at 5.5 GPa gradually changed to new spectrum during compression process. During decompression, back transformation was observed at 1.5 GPa, and original spectrum of phase III was observed again. For phase IV, a transition was found at 2.5 GPa for both compression and decompression processes. For phase II, new spectrum appeared at about 13 GPa during compression process, but peaks were broad, possibly due to non-hydrostatic condition. Change of Raman spectrum at each transition was discontinuous, so these transitions should be 1st order in nature.

Present in-situ Raman spectroscopic studies confirmed that phases III and IV are indeed retrograde phases. Observed transition pressures were lower than their supposed stable pressure region, consistent with previous quench experiments (Syono et al., 1971). These results were consistent with our first-principles study too. However, for phase transition of III, octahedral Si is expected for high-pressure phase. Rather low observed transition pressure (5.5 GPa) suggests that the transition is not same as that observed by first-principles calculation.

Currently, structural identification of high-pressure phases is underway by calculation of Raman spectra of candidate phases from first-principles.

Reference:

Liu, X., Kanzaki, M., Xue, X. (2013) Crystal structures of Zn_2SiO_4 III and IV synthesized at 6.5-8 GPa and 1,273 K, *Phys. Chem. Minerals*, **40**, 467-478.

Syono, Y., Akimoto, S., Matsui, M. (1971) High pressure transformations in zinc silicates, *J. Solid State Chem.*, **3**, 369-380.

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